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Observations of dislocation behaviour on different crystallographic faces of solution-grown sodium sulphate single crystals by chemical etching

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Abstract · Solution-grown anhydrous Sodium Sulphate (SS) single crystals with chemical formula Na_2SO_4 are analyzed by X-ray powder diffraction and chemical etch techniques. X-ray diffraction reveals the lattice structure belonging to orthorhombic system with lattice parameter values, in good greement with the reported ones. Optical microscopic observations of dislocation behaviour in several crystallographic faces namely {011}, {111}, {101} and {010} of SS by chemical etch technique are reported with greater details. The main features observed are the pyramidal pits, square pits, octagonal pits, low angle tilt boundary, extended rows of triangular pits, liquid inclusions, edge and screw dislocations *etc* It is found that solvents in presence of an additive, form well-defined dislocation pits The results are briefly analyzed from Cabrera's thermodynamic theory. In very few cases, Scanning Electron Microscopy shows a good correspondence between dislocation characteristics and observed etch pattern

Keywords · Single crystal growth, defects, etching, optical microscopy, inorganic compounds

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1. Introduction

Sodium sulphate (Na_2SO_4) (SS) is a chemical compound of ample interest and finds application in the field of synthetic detergent, manufacturing glass, textile dyes, tanning industries. A new market for sodium sulphate has now been developed in pollution control at coal plants. Moreover, salt cake (containing at least 97% Na_2SO_4) is used chiefly in wood digestion reagents in pulp and paper industries. Sodium sulphate has also found application in chemical industries. Research has developed new processes using SS to manufacture potassium and ammonium sulphate fertilizers, soda ash, sodium-bi-carbonate and caustic soda. SS is also used as a flux in the preparation of some anhydrous sulphates of amphoteric metals of lead and tin [1]. Anhydrous sodium sulphate is found in nature as the mineral Thenardite. Thenardite is generally fluorescent, showing a white colour in short-wave UV and yellow-green in long wave UV.

SS can crystallize in at least five different forms [2]. In the temperature range lower than 185°C, form V becomes stable and it corresponds to Thenardite. Thenardite (anhydrous SS) crystallizes in orthorhombic dispyramidal structure having point group $2/m\ 2/m\ 2/m$ and space group F_{DDD} with lattice parameters $a = 9.829$, $b = 12.302$, $c = 5.868$ Å and $Z = 8$ [3].

A number of investigations on SS including their growth and effect of impurity on their crystallization have been reported [4, 5]. At the same time, it is very essential to study the microstructural imperfections in revealing the dislocations sites in the as-grown crystals. But no report, till to-date, is available in this regard. For defect characterization, chemical etch technique being a simple but elegant tool to reveal dislocation sites in a single crystal, has been applied for the first time on different crystallographic faces of SS crystals. In continuation of our earlier works on few pure and mixed sulphates [6-12], we present here our recent results on structural studies and defect characteristics of SS crystal by X-ray powder diffraction and chemical etch technique. Etching behaviour on a number of crystallographic faces namely, {011}, {111}, {101} and {010} are investigated and reported here.

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2. Experimental

Single crystals of SS have been grown at an ambient temperature of $(35 \pm 1)^0$C by slow evaporation technique. A supersaturated solution of SS has been prepared at 35^0C using the pre-determined solubility data [13]. The solution was stirred constantly to avoid any spurious nucleation. It was then filtered and kept for evaporation in partly covered, high walled crystallization vessels The pH of the solution was maintained between 4 and 5. After 2-3 weeks, single crystals of SS having typical growth morphology have been harvested. The as-grown crystals are transparent having approximate dimensions $(8 \times 5 \times 3)$ mm^3.

X-ray powder diffraction (XRD) studies of SS crystals have been recorded at room temperature on a Philips microprocessor controlled X-ray diffractometer (APD 1710) with nickel-filtered CuKα radiation (λ = 1.5405 Å) and with an output power of (36 kV, 25 mA) obtained from highly stabilized X-ray generator PW 1130.

For etching studies, small transparent plates, parallel to different crystallographic orientations of few millimeters of thickness have been cut from the as-grown crystals and then polished using a mixture of 50:50 ethanol water solution. Following etchants have been employed for different timings at room temperature to reveal dislocations in SS system:

(i) ethanol-water solution of different concentrations,

(ii) $FeCl_3$ in HCl added to 80% ethanol water solution,

(iii) saturated solution of potassium acid pthalate (KAP),

(iv) saturated solution of sodium hydroxide (NaOH),

(v) minimum 35% HCl added to rectified spirit.

Etch patterns have been observed and photographed under an optical microscope (Carl-Zeiss, Jenavert).

3. Results and discussion

3.1 XRD studies :

X-ray powder diffractogram of pure SS has been recorded and analyzed using the computer program POWD [14] and it establishes that the crystal belongs to orthorhombic system with lattice parameter values ($a = 9.851$, $b = 12.341$, $c = 5.873$ Å) which, are in good agreement with the reported one [3]. Figure 1(a) and 1(b) show the typical growth morphology and X-ray diffractogram of pure SS respectively. Sharp intensity is observed from (040) reflection.

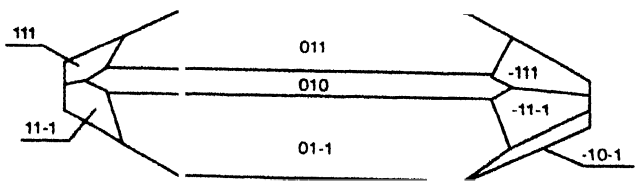


Figure 1. (a) Typical growth morphology of SS crystal.

3.2 Etching studies :

3.2.1 Slices parallel to {011}

Etching studies have been carried out on different crystallographic faces of SS. In order to clarify the origin of the

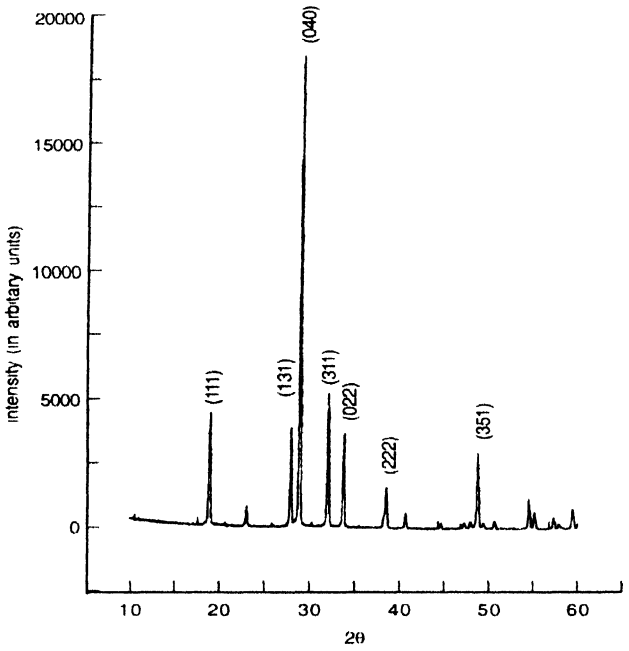


Figure 1. (b) X-ray diffractogram of anhydrous SS crystal

etch pits, alternating etching and polishing technique is a famous one. By this method, it is possible to track back the possible path of dislocation lines in a crystal [15]. Figure 2(a) illustrates the etch pattern produced by pure ethanol after 15 seconds of etching. It is a boundary produced by a number of pits and a precise observation shows it to be a symmetrically pure tilt boundary, may be formed by an array of edge dislocations, spreading one above another. Repeated polishing and re-etching does not change the etch pattern, which is very much prominent from the Figure 2(a′) and thus, it may be inferred that obviously the pits can be related to the line defects; dislocation outcrops at the surface [16]. With further increase in etching time, the pits lose their sharpness and distinctness, which may be attributed to the increase in tangential etching rate (V_l). Next, we have treated the crystal with different concentrations of ethanol-water mixture. Treatment with 75% ethanol-water solution produces few trapezium-shaped pits, which are also found on other crystallographic faces. Further dilution of the above mentioned etching solution can not produce any well-defined pits for this crystallographic face.

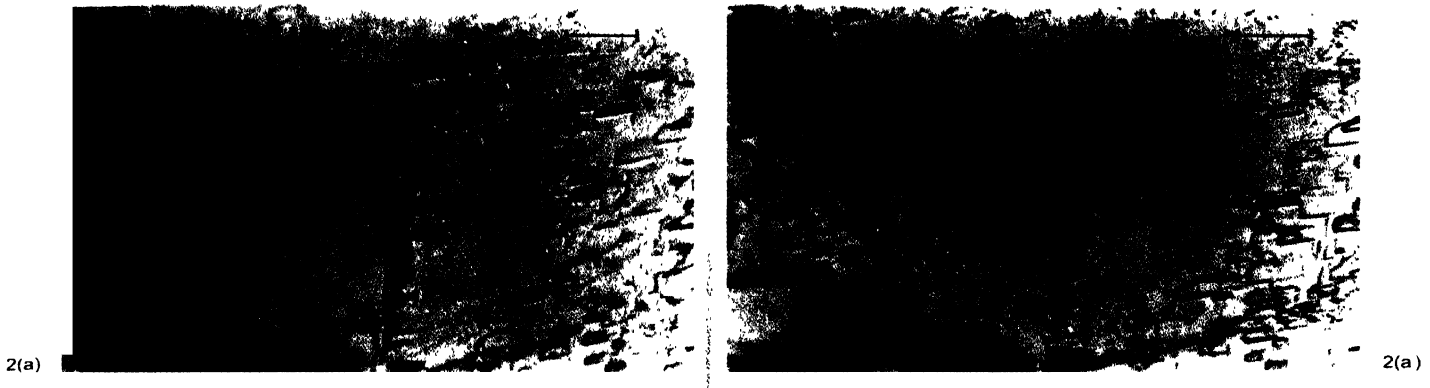


Figure 2. Etch patterns obtained on {011} faces of SS crystals in pure ethanol for (a) 15s and (a′) 45s (bar mark = 0.1 mm)

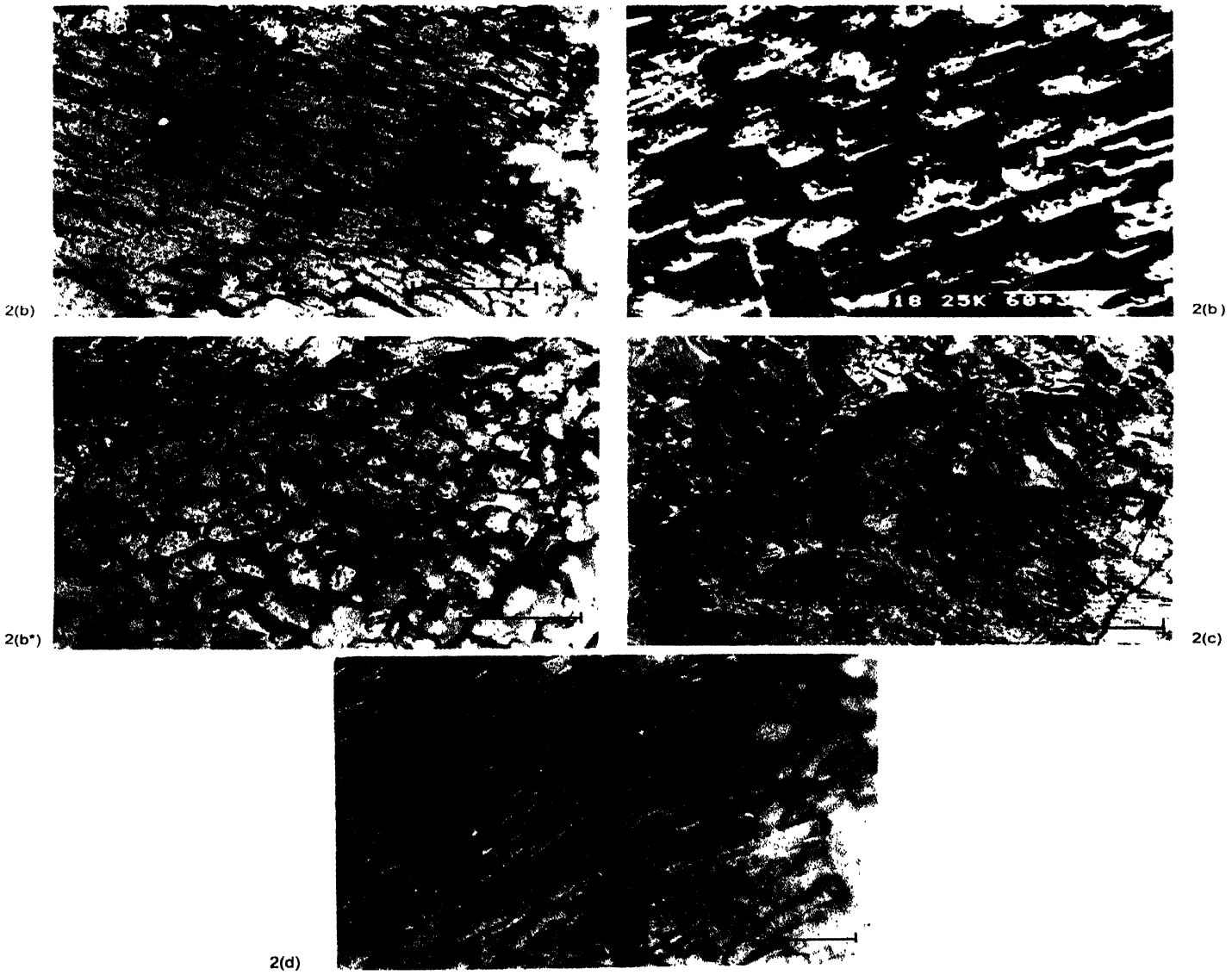
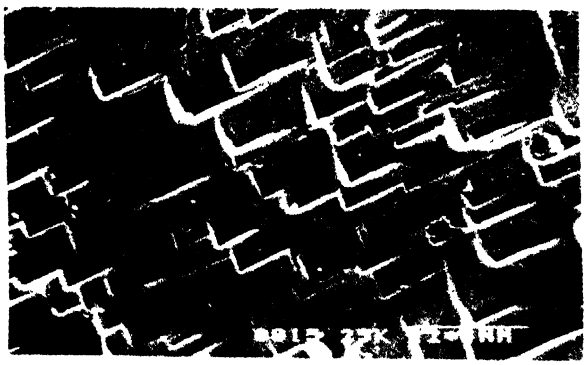


Figure 2. Photography of the surface of {011} faces after etching in $FeCl_3$ in HCl added to 80% ethanol-water solution after etched for (b) 45s, (b*) corresponding SEM, (b′) 3 minutes, (c) 3 minutes and (d) 3 minutes respectively (bar mark = 0.1 mm).

Figure 2(b) shows another interesting photograph of asymmetric pits slightly inclined to [011] while etched with $FeCl_3$ (in HCl) added to 80% ethanol-water solution for 45 seconds along with its SEM (Figure 2(b*)). With further increase in etch timings (3 minutes), the pits lose their sharpness at edges due to higher crystal solubility (Figure 2(b′)). Asymmetric pits are assumed to be produced at the emergent point of screw dislocation. Similar types of etch pattern were found earlier in the etching studies of LAP crystals [17]. With the increase in etch timings (3 minutes), another interesting etch-pattern has been observed. Pits here are trapezium in nature and they reveal the presence of both edge (pits E) and screw (pits S) dislocations (Figure 2(c)). It is seen that etch pits from screw dislocation are shallower (of little depth) than those for edge dislocations. The line drawn from the center of the base of the etch-pit to its apex is a tangent to dislocation line. For edge dislocations, the dislocation line is perpendicular to the surface whereas for screw dislocations, it makes an angle 45^0 with respect to the surface [18]. The difference in etching behaviour at screw and edge dislocations can be attributed to the difference in their energies, nature of the etchants used as well as the type of impurity added to the etchant [19-21]. A new type of etch-pattern has been obtained when etched for the same timing (Figure 2(d)). Here, morphologies of the pits are more or less triangular. Moreover, a row of closely spaced pits forming a boundary is also observed here. Formation of well defined etch pits depends on the dissolution rate (crystal solubility), which increases with the addition of impurity to the solvent. Doping of $FeCl_3$ plays an important role in formation of well-defined pits. Here, the liberated Fe^{3+} ions poison the kink sites, as a result the tangential displacement velocity, *i.e.*, V_t decreases whereas normal dissolution rate (V_n) at which, the pit deepens, remains unaffected and hence promotes the formation of well-defined pits [22, 23].

2(e)



2(e*)

Figure 2. Morphology on {011} faces after etching in saturated solution of KAP for (e) 90s and (e*) its corresponding SEM (bar mark = 0.1 mm).

Figure 2(e) illustrates the etch pattern produced by etchant 3 after 90 seconds of etching. Several extended rows of triangular pits inclined slightly to [011] direction indicating rows of dislocation lines are clearly observed in this figure and they can be related to low angle boundary [15, 24]. Figure 2(e*) shows the corresponding SEM micrograph. For a given crystal face, a high solubility results in a lower edge free energy and consequently, in easy etch pit formation at dislocations. Similar type of etch patterns were also observed earlier in etching studies of ADP crystals [16, 25].

When the same faces of SS have been etched with etchant 4 for a very short period (say 15s), a highly dense triangular pits appear on the surface (Figure 2(f)). With the increase in etch timing (4 min) density of the pit decreases but the pits also get flattened and few of them converted to pyramidal pits, marked P (Figure 2(f′)). The flattening of the etch pits may be contributed to the change in relative rates of dissolutions at dislocation sites along normal and lateral directions. During prolonged etching with saturated solution of NaOH, V_t of the surface steps increases compared to V_n resulting in the flattening of the observed pits. Another interesting pattern of liquid inclusions has been found after 2 minutes of etching in the same solvent (Figure 2(g)). These pits are produced due to trapping of etching media on the crystal surfaces. In the case of solution-grown crystals, the cause of formation of dislocation is often liquid inclusions in them.

3.2.2 Slices parallel to {111}

Treating {111} faces of SS with pure ethanol, could not produce any well-defined pits. Rather an interesting pattern of trapezium shaped pits is obtained after etching in 75% ethanol-water solution for 45 seconds. Treatment of the same face by 50% ethanol-water solution for 45 seconds produces row of pyramidal pits slightly inclined to [111] direction (Figure 3). Similar features are also found on {011} faces (Figure 2(f′)). With increase in etch timing, the pit flattens and loses its sharpness as observed

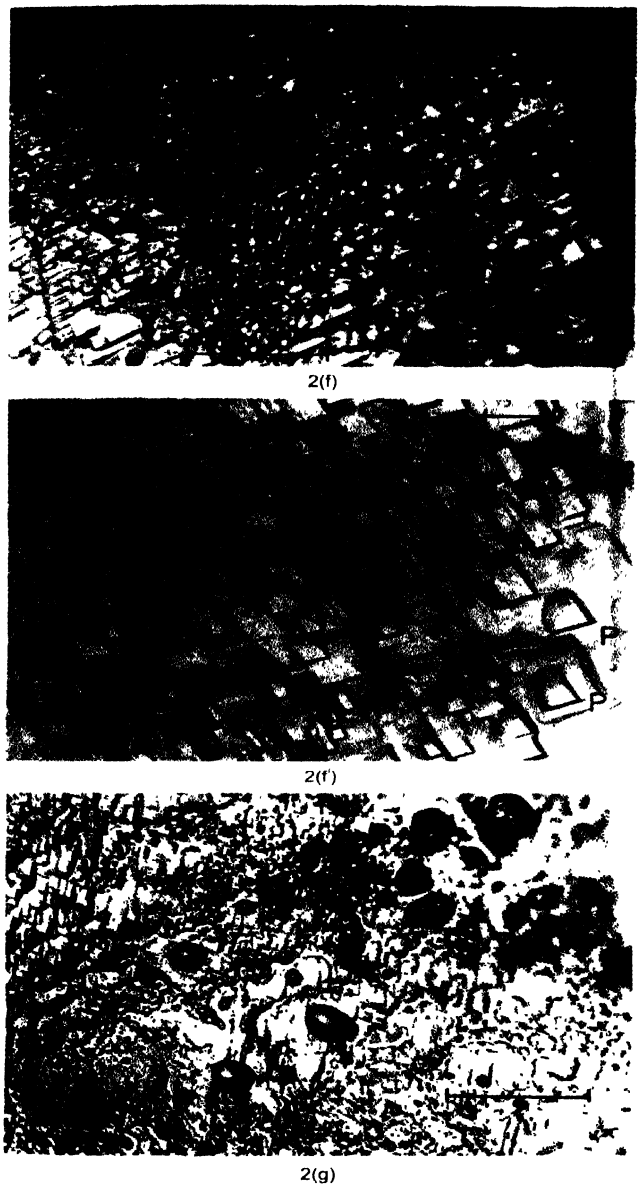


Figure 2. Etch micrograph by saturated solution of NaOH for (f) 15s, (f') 4 min and (g) 2 min (bar mark = 0 1 mm).

earlier. The density of pits initially decreases and then becomes constant, which may be attributed to the decrement of dissolution rate. Treatment of any other etchants cannot produce any other interesting etch pits.

3.2.3 Slices parallel to {101}

Similar to {111} and {010} faces, etching with pure ethanol could not produce any well-defined pits in this crystallographic face. Moreover, the effect of additive to the etching solution is also very much prominent on this surface. Similar to {011} faces, addition of the poison (Fe^{3+}) has marked effect to improve the etching power of the ethanol-water solution (Figure 4). Pits here are square in nature and they reveal the presence of dislocations in the as-grown crystal. Pits here have sharp edges and lateral widening is reduced.

Figure 3. Morphology on the {111} surfaces after etching in 50% ethanol water mixture for 45 s (bar mark = 0 1 mm)

Figure 4. Typical etch patterns on {101} faces of SS after etching in $FeCl_3$ in HCl added to 80% ethanol-water solution for 1 min (bar mark = 0 1 mm)

Figure 5. Etch pattern found on {010} faces of SS by minimum 35% HCl added to rectified spirit for 35 s of etching (bar mark = 0.1 mm).

3.2.4 Slices parallel to {010}

When {010} faces of the SS crystal are treated with the etchant 5, several octagonal pits have been obtained (Figure 5). The outer morphology of the pits reflect the symmetry of the face on which they occur and they overall, reveal the orthorhombic symmetry of the SS system and it is also confirmed by XRD as observed earlier by us in case of pure AS [6].

The change in etch pit density, pit size and pit morphology are normally associated with the lateral etch rate which, initially increases and then shows a rapid decrease possibly due to the formation of surface layer of reactant product [26, 27]. Experimentally observed relation between solubility of a crystal in a solvent and ability of formation of well-defined pits can be explained in terms of Cabrera's thermodynamic theory [28-30]. According to this theory, there is a particular value of undersaturation above which there is no barrier for etch-pit formation and a dislocation opens up spontaneously and microscopic dislocation etch pits are formed. Fast etchants like saturated solution of KAP, saturated solution of NaOH *etc.* can produce etch pits very easily. Pure ethanol which is a slower etchant, unable to produce well-defined etch pits even after a long period of etching. However, when ethanol-water solution of different concentrations are used as etchants *i.e.*, when the dissolving power of pure ethanol is increased by adding water, the undersaturation barrier to etch pit is overcome and optically visible etch pits are found under the microscope (Figure 3). Moreover, addition of an impurity ($FeCl_3$ in HCl in ethanol-water solution) plays a vital role for revealing dislocation etch pits (Figures 2(b-d), 4). The relation between the free energy change (ΔE) required for the formation of an dislocation etch pit and difference in chemical potential ($\Delta\mu$) of a crystal unit can be given as

$$\Delta E = 2\pi hr\gamma - \pi r^2 h\Delta\mu/\Omega - hA\alpha \ln(r/r_0), \qquad (1)$$

where $A = Gb^2/4\pi$, G is the shear modulus of the crystal, b is the Burgers vector of the dislocation, r and h are the radius and height of the etch pit respectively, r_0 is the radius of the dislocation core, γ is the edge free energy of the dissolution unit, Ω its molecular volume and α is the surface entropy factor. It is clear from this equation that for a particular crystal with constant G, b and Ω, impurity segregation at dislocations leads to an increase in chemical potential ($\Delta\mu$) and consequently decrease in ΔE. Addition of an impurity (Fe^{3+} ion) at dislocation, enhances nucleation rate along dislocation line (i.e., increasesd V_n) due to the presence in localized energy, minimizes the rate of movement of dissolution ledges away from the dislocation sites (ledge mobility factor) and hence, facilitates the formation of well-contrasting dislocation etch pits more easily [31]. Further, Honess [32] and Buckley [33] have stated that the etch pits produced by different solvents on the same face or by the same solvent at different concentrations may change in form, but they invariably reveal the symmetry of the surface on which they occur and here it is also true for SS system.

Table 1. Etching characteristics on different crystallographic faces of single crystals of sodium sulphate

Face	Etchant	Timings	Feature	Figure No
{011}	Pure ethanol	15 seconds	Boundary	2(a)
		45 seconds	-do-	2(a′)
	75% ethanol-water solution		Trapezium-shaped pits	--
	$FeCl_3$ in HCl added to 80% ethanol-water solution	45 seconds	Asymmetric pits	2(b)
			Corresponding SEM	2(b′)
		3 minutes	Asymmetric pits	2(b′)
		3 minutes	Trapezium-shaped pits revealing the presence of serew and edge dislocation	2(c)
		3 minutes	Triangular pits forming boundary	2(d)
	Saturated solution of KAP	90 seconds	Extended rows of triangular pits	2(e)
			Corresponding SEM	2(e′)
	Saturated solution of NaOH	15 seconds	Highly dense triangular pits	2(f)
		4 minutes	Triangular pits along with some pyramidal pits	2(f′)
		2 minutes	Liquid inclusion	2(g)
{111}	75% ethanol-water solution	45 seconds	Trapezium-shaped pits	–
	50% ethanol-water solution	45 seconds	Rows of pyramidal pits	3
{101}	$FeCl_3$ in HCl added to 80% ethanol-water solution	1 minute	Square shaped pits	4
{010}	Minimum 35% HCl added to rectified spirit	35 seconds	Octagonal pits	5

4. Conclusions

On the basis of the results of etching studies on solution grown SS crystals, it may be concluded that:

(i) All the above-mentioned chemical etchants have successfully revealed the presence of dislocation of different types in the crystal.

(ii) Some of the pit patterns do not depend on the choice an etchant and undersaturation of crystal faces. Pit shapes are directly related to the intermolecular forces within the crystal.

(iii) Most of the etch patterns found on different crystallographic faces of SS reveal the orthorhombic symmetry of the system, which is also confirmed by XRD studies.

(iv) There is always an undersaturation barrier to etch pit formation for particular faces. For fast etchants, dislocation opens up spontaneously and easily etch pits are formed. For pure ethanol, slight dilution is required to produce visible etch pits under optical microscope.

(v) From the overall etching studies on SS, it may however, be concluded that SS crystal grows mainly by dislocation-growth mechanism and etching studies on different crystallographic faces reveal that apart from few new patterns namely square pits, octagonal pits *etc.*, characteristic of particular faces, some common etch patterns namely trapezium-shaped pits, triangular pits are also found to occur which are independent of the choice of the crystallographic faces.

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